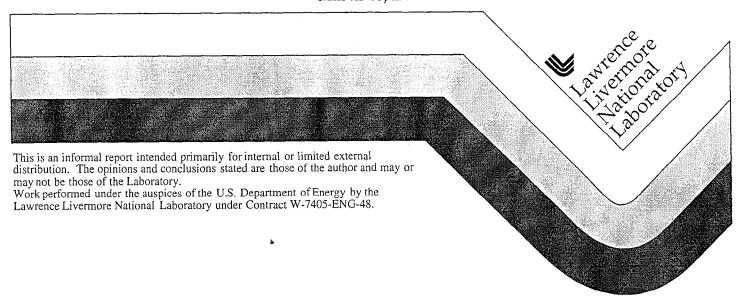
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March 26, 1999



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Final Reconnaissance Report

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EXECUTIVE SUMMARY

This preliminary report summarizes results from isotopic data recently generated on water collected for the West Basin Municipal Water District (WBMWD). Samples comprised monitoring and production wells up to 3.5 miles from the injection barrier, in addition to barrier product and blend water. The preliminary conclusions based on these data include:

- As define by δ^{18} O values, groundwater shows variable mixtures between pristine, local recharge and State Water Project water imported and injected into the barrier. One sample (747J) appears to be nearly 100% Colorado River water.
- Product water had a distinguishably low $\delta^{18}O$ value, but blending before injection may make it relatively indistinguishable from a typical Colorado River water. A δD analysis paired with the $\delta^{18}O$ may help better delineate between these sources.
- Low-level MTBE measurements (detection limit = 15 parts per trillion) suggested small amounts of young water (<5 yrs) were mixed in with older groundwaters.
- Groundwater ³H-³He ages ranged from 4 to 35 years old, with the oldest occurring in production wells. Ages 4 to >20 years were found in a monitoring wells close to the injection barrier.
- Groundwater ages generally increased with increasing distance from the injection barrier.
- Radiocarbon (¹⁴C) concentrations of dissolved inorganic carbon measured in two production wells suggest recharge ages thousands of years old.
- The ³H-³He ages of groundwater suggest that horizontal transport rates range from <100 to 460 ft/yr. Over the 2 miles of distance and 35 years of transport time suggested by the data, >50 percent dilution appears to have occurred. However, groundwater ages in wells near the injection barrier (4 to >20 years) do suggest flow is not uniform within the aquifer and preferred flow paths with more rapid transport rates may exist.

INTRODUCTION

The WBMWD produces 7.5 million gallons of recycled water per day utilizing lime clarification, microfiltration, and reverse osmosis technologies. Annually, ~5000 acre-ft of this recycled water, or product water, is used to prevent seawater intrusion by direct injection into the West Basin Barrier Project located in southwestern Los Angeles County. 18,000 acre-ft are injected annually into the barrier, of which most comprises Metropolitan Water District imported water supplies (State Water Project and Colorado River Water).

Proposed California state regulations on treated waste water recharged into groundwater aquifers subsequently used for drinking water requires 1) at least a one year subsurface residence time, 2) a \geq 50% dilution of recycled water by water of a non-waste

water origin, and 3) a recycled water TOC concentration of ≤1.0 mg/L (State of California, 1993). Currently, product water produced by WBMWD is appropriately blended with imported water before injection. However, in the near future WBMWD would like to replace much of the imported water used for injection with recycled water, which would significantly reduce the necessary blending before injection. Consequently, WBMWD would rely on mixing in the aquifers during transport away from the injection barrier for the necessary blending.

WBMWD contracted with Lawrence Livermore National Laboratory (LLNL) to help delineate ages and mixing of groundwater in monitoring and production wells near the injection barrier. Methodologies of isotope tracing developed by LLNL have successfully demonstrated age and mixing determinations in similar water reuse projects (Hudson et al., 1995, Davisson et al., 1998). In this report, we utilize measurements of tritium (³H), dissolved helium isotopes (³He and ⁴He), oxygen-18 (¹⁸O) of the water, radiocarbon (¹⁴C) of dissolved inorganic carbon, and low-level methyl-tert-butyl ether (MTBE) measurements to delineate ages and mixing for sampled wells. Detailed discussion of these research methodologies have been included in an appendix.

METHODS

A total of 13 samples were collected (see Table 1 and Fig. 1). Five samples were production wells, 5 were monitoring wells, and 3 were injection waters. The latter include product water, MWD water used for blending, and blended water in the distribution line. Sample points were distributed along the length of the injection barrier, and ranged from very near to injection points to ~3.5 miles away. Samples were focused on wells completed in the Silverado Aquifer, although exact completion depths of some production wells are unknown.

Samples were collected by LLNL and WBMWD staff. Groundwater was collected directly from submersible or immersible pumps. Injection waters were collected from faucet taps. Samples for helium and other noble gases were collected in 3/8 inch copper tubing by creating a laminar flow through the tube, which is connection to the pump or faucet, and crimping down on steel pinch clamps to trap an air-free water sample in the copper tube. The ¹⁸O samples were collected in a 30ml glass bottles with an air-tight polyseal cap. Samples for ¹⁴C were collected in a 125ml teflon-capped bottles and poisoned with a few drops of HgCl₂. Samples for MTBE were collected in ultra-clean 40ml VOA vials. Trip blanks were used for the MTBE by exposing MTBE-free water in a VOA vial to the atmosphere for an amount of time equivalent to sampling. Trip blanks showed no measurable contamination.

The 18 O was measured with a standardized technique using the CO₂ equilibration method (Epstein and Mayeda, 1953). The extraction method results in purified CO₂ gas that was analyzed on a VG Prism isotope ratio mass spectrometer at LLNL. The isotope abundance is measured as a ratio to the more abundant 16 O. This ratio is normalized to an internationally recognized standard (SMOW or Standard Mean Ocean Water) and converted to a parts per thousand scale, whereby δ^{18} O = (Rsample/Rstd-1)1000, where R is the 18 O/ 16 O ratio.

Tritium is analyzed by the helium-accumulation method (Surano et al., 1992), where water samples are cryogenically degassed, sealed, and stored for 15-60 days to allow

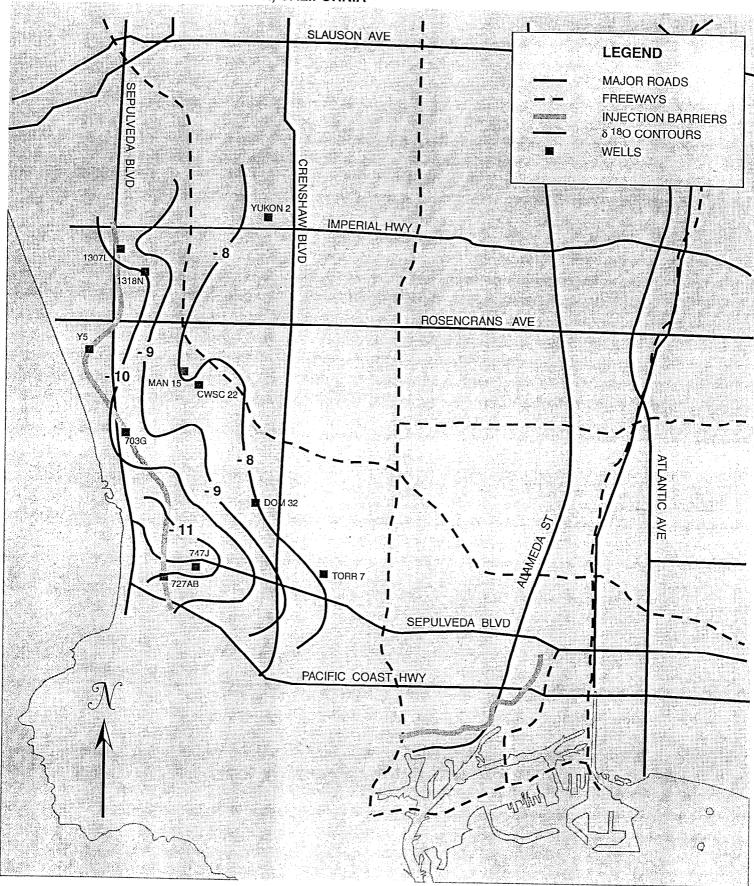


Figure 1. Well locations and $\delta 180$ contours of groundwater samples show that the $\delta 180$ values increase with increasing distance from injection barrier.

accumulation of 3 He from the tritium decay. The 3 He is subsequently degassed, purified, and quantified on a VG-5400 noble gas mass spectrometer. The 3 H concentration is reported as picocuries per liter (pCi/L; 1.0 pCi/L = 2x104 3 H atoms/g H₂O).

The copper tubes for the dissolved noble gas measurements are vacuum fitted to an evacuated container. The copper cold seal formed during sampling is uncrimped and the water sample is released into the evacuated container where the water sample is subsequently degassed and the noble gases of interest are isolated and analyzed on a VG-5400 noble gas mass spectrometer.

The MTBE was measured by purge-and-trap gas chromatography methods under ultraclean conditions, followed by ion-selective mass spectrometry.

The inorganic carbon was acid stripped under high vacuum and purged with an ultra pure carrier gas. The liberated CO_2 was then reduced to graphite on a separate vacuum line using a cobalt catalyst and hydrogen gas at a 570°C reaction temperature. All ^{14}C concentrations were determined on the accelerator mass spectrometer at LLNL. The ^{14}C results are reported as a percent modern carbon (pmc) relative to a NBS oxalic acid standard, which represents the ^{14}C concentration of atmospheric CO_2 in 1950, before large-scale atmospheric testing of nuclear weapons commenced. Apparent ages are calculated using a half-life of 5730 years. The $^{13}C/^{12}C$ ratio was also determined on the dissolved inorganic carbon, and it is normalized to a standard similar to the ^{18}O and reported in $\delta^{13}C$ notation.

RESULTS AND DISCUSSION

Recharge Sources

Recharge sources can be delineated using the $\delta^{18}O$ measurements (see Fig. 1). Measured values range from -7.1 to -13.4 per mil. The highest $\delta^{18}O$ values between -7.1 and -7.9 were measured in production wells MAN-15, Torrance-7, and SCWS-Yukon-2, while slightly lower values (-8.0 and -8.9 per mil) were measured in Dominguez-32 and CWSC-22. The highest value (-7.1 per mil) is consistent with values observed and expected for local precipitation recharged in coastal areas of California (Ingraham and Taylor, 1991; Williams, 1997; Davisson et al., 1998).

Injection water (Y5BB) had a significantly lower δ^{18} O value (-12.1 per mil). This water comprised a mixture of product water ("BPW Final" in Table 1), which had the lowest δ^{18} O value of -13.4 per mil, and MWD water, which was -11.3 per mil. A simple mass balance among these end-members and the blended water indicates a 38% mixture of product water in the blend. The MWD water is likely either from a Colorado River or State Water Project source. Colorado River varies in δ^{18} O from approximately -13.5 to -11.0 per mil (Williams, 1997), depending on where it is sampled. Modern Colorado River usually has a high conductivity, while in the past conductivity was significantly lower. State Water Project water has a range in δ^{18} O from an estimated -11.5 to -9.0 per mil. Direct measurements are scarce and this range is derived from δ^{18} O values observed in the Sacramento-San Joaquin Delta, and from turnouts in San Bernadino County (unpublished data). The -11.3 per mil value for the MWD water is consistent with both

State Water Project and Colorado River. However, the low conductivity of the MWD water suggests a State Water Project source.

The δ^{18} O values in monitoring wells (-9.3 to -12.0 per mil) were lower than in the production wells. This indicates that the monitoring wells comprised a larger proportion of injected water compared to the production wells. Monitoring wells are located geographically closer to the injection barrier. Figure 1 and Figure 2a show that the δ^{18} O values of groundwater increase with increasing distance from the barrier, consistent with eastward transport of low δ^{18} O injection water and mixing with a higher δ^{18} O groundwater recharged from local precipitation. The data in Figure 2a suggests that mixing occurs primarily between a local groundwater with a -7.0 per mil value and injection water of around -11.0 per mil. The exception is in monitoring well 747J, which has a δ^{18} O value of -12.0 per mil. Based on 3 H concentration and age determination, our tentative conclusion is that this groundwater is Colorado River recharge (see below). The low δ^{18} O value of the product water was recently introduced into injected water, and its influence on the δ^{18} O values of groundwater are clearly lacking in this data set.

Uncertainties in these interpretations are controlled by our lack of knowledge of end-member $\delta^{18}O$ values. Local precipitation recharge may be variable geographically in this area, and our data is limited to just one or two analyses. In addition, the $\delta^{18}O$ value of the injected water may likely vary over time, due to changing sources of imported water (i.e. Colorado River vs State Water Project).

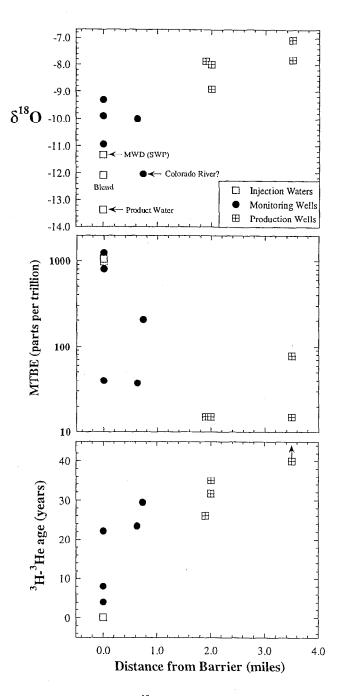


Figure 2. The δ^{18} O, MTBE, and groundwater age all systematically vary with distance from the injection barrier. These variations are consistent with mixing between recent injection water and older groundwater derived from local precipitation.

Groundwater Ages

Tritium concentrations in the samples were variable from 0.2 to 377 pCi/L. Production well SCWS-Yukon-2 had no measurable ³H, and well Torrance-7 only had a trace. Based on the lack of ³H and ³He from ³H decay in these samples, these wells have groundwater ages effectively >40 years old. Both of these samples also had an appreciable level of dissolved ⁴He, which indicates native groundwater possibly

thousands of years old. No other samples show elevated levels of ⁴He (see ³He/⁴He ratios in Table 1).

All other samples had ³H concentrations >20 pCi/L, suggesting a significant mixture of groundwater <40 years old. This includes all the other production wells. When combined with the ³He measurements, calculated ages range between 4 and 35 years. These ages are "apparent ages" since groundwater samples may be mixtures of very young water and somewhat older water (<40 years), which would both have ³H and ³He. The ³H-³He dating method cannot separate ages in mixed samples.

The groundwater ages generally increase with increasing distance from the injection barrier (Fig. 2c). However, groundwater sampled from monitoring wells within close proximity to the barrier (e.g. 703G, 727AB, and 1307L) had ages from 4 to 22 years old. These older ages close to the recharge point suggest that mixing is appreciable within a few hundred feet of the barrier. Alternatively, much of the mixing could take place within the well casing due to long intervals of perforation screen.

We can calculate what the ³H concentration was at the time of recharge by adding the measured ³H with the measured ³He. In doing so, we calculate initial ³H concentrations between 26 and 2049 pCi/L. The latter concentration was calculated from well 747J, which we earlier interpreted as a Colorado River recharge source. The high initial ³H combined with the 30 year old age is consistent with ³H concentrations in precipitation accumulated in the Rocky Mountains in the late 1960s. All other initial ³H concentrations are much lower (26 to 420 pCi/L), and combined with their groundwater ages are consistent with ³H concentrations in California precipitation.

Measurements of ¹⁴C were performed on 5 samples, which include the barrier blended water, two monitoring wells (703G and 1318N), and two production wells (Dominguez-32 and SCWS-Yukon-2). The production wells had the lowest ¹⁴C concentrations of 47 and 53 pmc. The monitoring wells were 74 and 95 pmc, while the injection water was 75 pmc. The ¹⁴C of the injection water is surprisingly low, but can be explained by low ¹⁴C concentration in CO₂ introduced during recarbonation of the treated waste water. The 95 pmc in one monitoring well is consistent with recent recharge (8 years in this case), while the 74 pmc of the other monitoring well suggests a mixture of older groundwater (>1000 years old). Alternatively, the inorganic carbon of injected water could have reacted with ¹⁴C-absent CaCO₃ in the aquifer material, causing a decrease in dissolved ¹⁴C concentrations of the groundwater. The low ¹⁴C in production well SCWS-Yukon-2 is consistent with old recharge (>1000 years old), since this sample was ³H-absent, suggesting no injection water has reached this well. The low ¹⁴C in Dominguez-32 also suggests older recharge, but this also may be controlled by its high TDS conditions (seawater intrusion), since mineralization of ¹⁴C-absent organic matter is known to occur in areas of seawater intrusion (Hudson et al., 1995). Note that the ¹⁴C concentration has a simple linear correlation with the dissolved inorganic carbon and the δ^{13} C (see Table 1), suggesting conservative mixing between two end-members similar to the δ^{18} O.

Groundwater Mixing

The δ^{18} O values and 14 C concentrations suggest that most groundwaters are mixtures of old recharge from local precipitation with barrier injection water of more recent age. We can estimate mixing between local recharge and injected water by assuming a two end-member mixing model with δ^{18} O values of -7.1 per mil for local recharge and -11.3 for injected water. The percent of injected water in a groundwater would follow the equation

Percent injected water = 100 x
$$\left(\frac{\delta^{18}O_{mix} - \delta^{18}O_L}{\delta^{18}O_I - \delta^{18}O_L} \right)$$

where subscripts mix, I, and L are respectively the measured value, the injection water (-11.3 per mil), and the local recharge value (-7.1 per mil). Below are the calculated mixtures. Product water, the blended water, and 747J are not included because their sources are unrelated. Note that production wells have the lowest mixture of injected water. The confidence in these mixtures is not high due to the limited data. Nevertheless, these preliminary results suggest that >50% dilution of injected water occurs before reaching production wells.

Injection Waters MWD-1 BPW FINAL Y5BB	Percent Injected Water imported water 100% recycled blend water
Monitoring Wells	
703G	53
1318N	69
727AB	91
747J	-
1307L	67
Production Wells	
MAN-15	19
TORRANCE 7	17
DOMINGUEZ 32	21
SCWS-YUKON 2	0
CWSC 22	43

Additional evidence for mixing can be gleaned from the MTBE measurements. MTBE has been used as a gasoline additive since 1996 and comprises 11% by volume all domestic gasoline consumed. Recent observations of water supplies throughout California have noted low-levels of MTBE (1-5 parts per billion). Our measuring techniques allows us to measure down to 15 parts per trillion. At these low levels, the MTBE may provide an indicator of recent groundwater recharge (e.g. <5 years old) mixing in small proportions with older groundwater. In addition, we expect to see an

inverse correlation between MTBE concentration and groundwater age, due to recent increase use of MTBE. In figure 3 below, MTBE measured in the water samples for this study show a general inverse correlation with age. Note the 4 groundwater samples with $^3\text{H-}^3\text{He}$ ages >20 years old that have measurable MTBE. Assuming this MTBE is related to recent sources (injected water, leaking underground fuel tanks, etc.), the data would suggest that small amounts of recent recharge with MTBE contamination mixes in with some of the older groundwater. The mixtures are small enough that they are imperceptible with respect to the $\delta^{18}\text{O}$ data. However, some uncertainty still exists as to whether older MTBE sources (before 1996) may be present in the subsurface of this area.

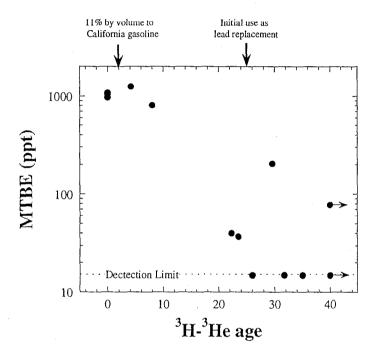


Figure 3. The MTBE shows an inverse correlation with groundwater age, reflecting recent increase use of MTBE. However, note that 4 groundwaters with ages >20 years have measurable amounts of MTBE, suggesting small mixtures of young (<5 years) groundwater.

Groundwater Transport Rates

We can derive groundwater velocities from the ³H-³He age data. By simply dividing the groundwater age into the distance of the well from the injection barrier, we derive the linear velocity of the groundwater. Since the ages are "apparent ages", it follows that the velocities are also "apparent" transport rates. The velocities may comprise a mixture of fast and slow flow paths, corresponding to high permeability and low permeability zones in the aquifer. Below are listed calculated velocities.

Monitoring Wells	feet/year
703G	<100
1318N	140
727AB	<100
747J	130
1307L	<100
Production Wells	
MAN-15	390
TORRANCE 7	460
DOMINGUEZ 32	330
SCWS-YUKON 2	460
CWSC 22	300

The results suggest a range in linear velocities of at least a factor of five. Similar transport rates were calculated for the Talbert Gap injection barrier in Orange County (Hudson et al., 1995). Exact distances of monitoring wells 703G, 727AB, and 1307L were not known at the time this report was written. Therefore, <100 ft/yr is a best estimate.

CONCLUSIONS AND RECOMMENDATIONS

Sources of groundwater recharge can be delineated with $\delta^{18}O$ measurements. However, blended product water has a $\delta^{18}O$ value that overlaps Colorado River values and will not be easily distinguishable. Analysis of the deuterium in water samples may provide an added tracer that will help further delineate blended product water from Colorado River water and State Water Project water. The higher $\delta^{18}O$ value of local recharge derived from precipitation is easily distinguishable from injected water.

The local recharge also has an old age (>1000 years old) as distinguished by low 14 C concentrations and appreciably little 3 H and radiogenic 3 He. Injected water ranged from 4 to 35 years old, with increased age correlating with increasing distance from the injection barrier. Lateral transport rates calculated from the ages suggest <100 to 460 ft/yr. Mixing is also important, and based on a δ^{18} O mixing model, injection water mixed in production well water is >50% diluted with old groundwater recharged from local precipitation.

The low-level MTBE analysis indicates that at least one production may have a small mixture of young groundwater (<5 years old). All the monitoring wells had measurable MTBE levels, suggesting mixing of young water. Further delineation of young groundwater mixtures in wells, particular groundwater <1 year old, is difficult with the existing data. It is recommended that introduction of an artificial tracer, such as an isotopically enrich Xe, into the injection water would provide definitive proof of groundwater <1 year old in key wells.

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Table 1

WEST BASIN MUN	IICIPAL WA	TER DISTRICT, LA: ISOTOPES		T						!	
no measurement				1							
ND = No Detect											
MW = Monitoring w	ell, PD = Pro	oduction well, SW = Surface water									
FIELD MEASUREN	MENTS	FIELD DATA									
SAMPLE	DATE	WELL TYPE, INFO	DEPTH	PERF.	Water Level	COND.	Ph	TWATER	DO _{WB}	DO _{LLNL}	Cl ₂
		WELL THE, IIII O	(FEET)	(FEET)	(FEET)	(μS)		(°C)	(mg/L)	(mg/L)	(mg/L) _{total}
703G	06/01/98	MW, El Segundo Blvd. groundwater, Silverado aq.	384	250-360	88	800.0	7.70	23.1	1.7	<1.0	0.16
1318N	06/01/98	MW, El Segundo maintenance yard groundwater, Silverado aq.	262	34-104	78.6	1100.0	7.64	25.0	2.1	2.00	0.12
MWD-1	06/01/98	SW, El Segundo maintenace yard municipal water				400.0	7.95	25.0	7.00	8.00	1.11
BPW FINAL	06/02/98	SW, WB Recclamation plant barrier product water				380.0	8.28	22.8			
Y5BB	06/02/98	SW, Manhattan Beach barrier blend				600.0	7.80	20.8	7.2	8.00	
MAN 15	06/02/98	PW, Silverado aq.				920.0	7.44	22.7	2.7	1.00	
TORRANCE 7	06/02/98	PW, Torrance, H ₂ S present groundwater, Silverado aq.				830.0	7.99	25.1	1.8	<1.0	
727AB	06/08/98	MW, H₂S present	375		84.6	500.0	7.85	25.0	1.70		1.43
747J	06/08/98	MW	466		73	500.0	7.63	22.2	1.9		0.78
1307L	06/11/98	MW	252		103.7	600.0	7.63	19.1	2.0		0.62
DOMINGUEZ 32	06/11/98	PW, desalter influent				6500.0	7.54	25.0	0.9		0.94
SCWS-YUKON 2	06/10/98	PW				800.0	7.79	23.5	2.40		0.61
CWSC 22	06/10/98	PW, H₂S present				1000.0	7.60	22.6	1.5		1.45

Table 1

WEST BASIN MUN	ICIPAL WAT		1		 		T		·	T
no measurement										
ND = No Detect										
MW = Monitoring w	ell, PD = Pro		·				-			ļ <u></u>
FIELD MEASURE	MENTS			ISOTOPES						
SAMPLE	DATE	³ H	³ H- ³ He age	¹⁴ C	APP. AGE	$\delta^{13}C_{pdb}$	DIC	$\delta^{18}O_{smow}$	³H/⁴He	MTBE
		(pCi/L)	(years)	(pmc)	(years)	(‰)	(ppm HCO ₃)	(‰)		ppt
703G	06/01/98	23.0	8	94.9	431	-9.16	138.30	-9.32	1.13	807
1318N	06/01/98	108.0	24	73.7	2522	-13.64	188.00	-10.01	3.79	37
MWD-1	06/01/98		_			-6.62	127.10	-11,33	1.00	974
BPW FINAL	06/02/98	25.7	-			-30.17	94.60	-13.37	1.01	1080
Y5BB	06/02/98	26.0	-	74.9	2391	-11.58	120.10	-12.08	1.00	1050
MAN 15	06/02/98	20.0	26			-17.94	282.50	-7.88	1.41	<15
TORRANCE 7	06/02/98	1.9	>40			-9.42	365.70	-7.82	0.47	78
727AB	06/08/98	29.0	4			-10.93	128.00	-10.94	1.09	1260
747J	06/08/98	377.0	30			-10.60	174.90	-12.04	18.00	204
1307L	06/11/98	72.0	22			-11.50	170.70	-9.90	2.99	40
DOMINGUEZ 32	06/11/98	68.0	32	47.1	6230	-17.26	210.80	-7.99	3.58	<15
SCWS-YUKON 2	06/10/98	0.2	>40	53.0	5253	-17.94	260.40	-7.07	0.82	<15
CWSC 22	06/10/98	37.0	35			-15.13	234.90	-8.91	3.09	<15